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[Title of the Invention] ADHESIVE COMPOSTION

[Abstract]

[Purpose] To provide an adhesive composition comprising as a base polymer an olefinic polymer grafted with a silane compound which exhibits an excellent heat resistance and humidity resistance and thus can be suitably used particularly as an adhesive for glass.

[Constitution] An adhesive composition having from 20 to 70 parts by weight of a propylene-α-olefin copolymer having a melt index of from 3.0 to 4.5 as measured at 190°C incorporated in from 30 to 80 parts by weight of a base polymer composed of an olefinic polymer grafted with a silane compound to form a disperse phase having an average particle diameter of not greater than 80 μm.

[Claims]

1. An adhesive composition having from 20 to 70 parts by weight of a propylene-α-olefin copolymer having a melt index of from 3.0 to 4.5 as measured at 190°C incorporated in from 30 to 80 parts by weight of a base polymer composed of an olefinic polymer grafted with a silane compound to form a disperse phase having an average particle diameter of not greater than 80 μm.

2. The adhesive composition according to Claim 1, wherein

said olefinic polymer grafted with a silane compound is a silane-grafted modification of at least one olefinic polymer selected from the group consisting of ethylene-vinyl acetate copolymer, ethylene-ethyl acrylate copolymer and glycidyl group-containing polymer.

[Detailed Description of the Invention]

[0001]

[Industrial Field of Application]

The present invention relates to an adhesive composition and more particularly to an adhesive composition suitable particularly for use in an art requiring heat resistance as in the lamination of glass members and the fixing of parts.

[0002]

[Related Art]

A laminated glass for automobile, etc. is obtained by bonding two sheets of glass plates with a plasticized resin sheet as an adhesive interposed therebetween upon heating under pressure. A multi-layer glass for use in heat insulation and sound insulation is obtained by retaining two sheets of glass plates with an intermediate air layer interposed therebetween, bonding the two sheets of glass plates to a spacer such as metal with an adhesive, and then sealing the periphery thereof with a sealing material.

[0003]

Since glass has a silanol (Si-OH) group on the surface thereof, adhesives for glass comprise a polymer having a polar group such as -OH group, -COOH group, -CO group and -COOR group. The adhesives having such a polar group form a hydrogen bond or double bond with the silanol group in the surface of glass to give a firm bond.

[0004]

As a method for enhancing the adhesivity to glass or metal there has heretofore been known a method involving the graft copolymerization of an olefinic polymer with a silane compound. For example, adhesives obtained by grafting olefinic polymers such as ethylene-vinyl acetate copolymer (EVA) and ethylene-ethyl acrylate copolymer (EEA) with a silane compound have been proposed (Patent Publication No. 2-26660, Patent Publication No. 2-50147, Patent Application Disclosure No. 60-179483). These silane-grafted modifications react with the silanol group present on the surface of glass to exhibit a high adhesivity.

[0005]

However, referring to these adhesives comprising EVA, EEA or the like as a base polymer, the melting point of these polymers normally fall within the range of from about 60 to 100°C. Therefore, once applied to an adherend such as glass, these adhesives soften and show a drop of adhesivity that causes defectives such as slippage when put at an ambient temperature of not lower than 100°C under the application of force. Further, these adhesives show a drop of adhesivity at a high temperature and humidity.

[0006]

On the other hand, photo-setting adhesives cannot be easily subjected to slippage even at high temperature after curing. However, these adhesives are normally supplied in liquid form and thus can be difficultly handled and are unsuitable for filling relatively wide spaces.

[0007]

[Problems that the Invention is to Solve]

An object of the present invention is to provide an adhesive composition having enhanced adhesivity, heat distortion

resistance and humidity resistance at high temperature. Another object of the present invention is to provide an adhesive composition comprising as a base polymer an olefinic polymer grafted with a silane compound which exhibits an excellent heat resistance and humidity resistance and thus can be suitably used particularly as an adhesive for glass.

[0008]

The inventors made extensive studies of solution to the problems with the related art. As a result, it was found that by blending an olefinic polymer such as EVA and EEA grafted with a silane compound as a base polymer is blended with a propylene-α-olefin copolymer while being dispersed in admixture so that the propylene-α-olefin copolymer forms a fine disperse phase, the resulting product exhibits improved adhesivity, heat distortion resistance and humidity resistance at high temperature without impairing the adhesivity characteristic to the base polymer. The present invention has thus been worked out on the basis of this knowledge.

[0009]

[Means for Solving the Problems]

Thus, the present invention provides an adhesive composition having from 20 to 70 parts by weight of a propylene-α-olefin copolymer having a melt index of from 3.0 to 4.5 as measured at 190°C incorporated in from 30 to 80 parts by weight of a base polymer composed of an olefinic polymer grafted with a silane compound to form a disperse phase having an average particle diameter of not greater than 80 μm.

[0010]

The present invention will be further described hereinafter. Examples of the olefinic polymer to be grafted with

a silane compound include ethylene-vinyl ester copolymer such as ethylene-vinyl acetate copolymer, ethylene-unsaturated carboxylic acid ester copolymer such as ethylene-acrylic acid ethyl copolymer, ethylene acrylic acid butyl copolymer and ethylene-methacrylic acid methyl copolymer, ethylene-butene copolymer, and glycidyl group-containing olefinic polymer such as ethylene-vinyl acetate-glycidyl methacrylate copolymer and ethylene-ethyl acrylate-glycidyl acrylate copolymer.

[0011]

Preferred among these olefinic polymers are ethylene-vinyl acetate copolymer, ethylene-ethyl acrylate copolymer, and glycidyl group-containing olefinic polymer. When the glycidyl group-containing olefinic polymer is used to effect adhesion at high temperature, the adherend reacts with the epoxy group derived from the glycidyl group to enhance adhesivity. These silane-grafted modifications may be used, singly or in combination.

[0012]

Examples of the silane compound include unsaturated alkoxy silane compounds such as vinyl methoxy silane, vinyl triethoxy silane, vinyl tri(β-methoxyethoxy)silane, vinyl triacetoxy silane, acryloxy propyl trimethoxy silane and methacrylocy propyl trimethoxy silane.

[0013]

The method for the graft copolymerization of the olefinic copolymer with the silane compound is not specifically limited. In practice, however, there is preferably used an ordinary method involving melt mixing of an olefinic polymer and a silane compound in the presence of a radical polymerization initiator. The amount of the silane compound to be grafted on the olefinic copolymer is normally from about 0.2 to 4 parts by weight based

on 100 parts by weight of the olefinic polymer.

[0014]

In the present invention, a propylene-α-olefin copolymer having a melt index of from 3.0 to 4.5 at 190°C is dispersed in admixture with a base polymer made of the olefinic polymer grafted with a silane compound. In this case, the mixing and dispersion are effected such that the propylene-α-olefin copolymer forms a disperse phase having an average particle diameter of not greater than 80 μm in the base polymer.

[0015]

As the propylene-α-olefin copolymer there is preferably used one having a melting point of from 120°C to 160°C. When the propylene-α-olefin copolymer is dispersed in admixture with the base polymer such that a fine disperse phase is formed, the propylene-α-olefin copolymer doesn't begin to melt even when heated to a temperature in the vicinity of the melting point of the base polymer, causing a phenomenon that the propylene-α-olefin copolymer acts as if it fill the base polymer as a filler and hence making it possible to inhibit the heat distortion of the entire adhesive composition.

[0016]

A propylene-α-olefin copolymer is obtained by the copolymerization of a propylene with one or more C_4-C_{20} olefins (e.g., 4-methyl-1-pentene, 1-decene-, 1-hexene, 1-butene). Referring to the composition of the propylene-α-olefin copolymer, the content of propylene and α-olefin are normally from 10 to 85 mol-% and from 15 to 90 mol-%, respectively. A specific example of the propylene-α-olefin copolymer is one comprising

from 10 to 85 mol-% of propylene, from 3 to 60 mol-% of 1-butene and from 10 to 85 mol-% of other α-olefins.

[0017]

In the art of polymer blend, many studies have been made of relationship between dispersed state and physical properties of miscible system and nonmiscible system. However, no methods can confirm the relationship between the dispersed state and the physical properties of a blend of a specific polymer with other polymers but experimental method.

[0018]

For example, examples of the polymer having a melting point of not lower than 120°C besides the propylene-α-olefin copolymer include various polymers such as polyethylene and polyester elastomer. However, these polymers have no adhesivity to glass, etc. Therefore, when such a high melting polymer is dispersed in a base polymer made of an olefinic polymer grafted with a silane compound, the resulting product exhibits somewhat improved heat distortion resistance but loses somewhat the adhesivity characteristic to the base polymer. It is desired to improve the heat distortion resistance and high temperature adhesivity of the adhesive composition without deteriorating the adhesivity characteristic to the base polymer.

[0019]

The inventors made studies of various polymers. It was found that when a propylene-α-olefin copolymer having a melt index (MI) of from 3.0 to 4.5 as measured at 190°C is dispersed in admixture with the aforementioned base polymer such that a disperse phase having an average particle diameter of not greater than 80 μm is formed, the resulting adhesive composition exhibits remarkably improved heat distortion resistance as well as good

adhesivity at high temperature and excellent humidity resistance.

[0020]

Even a propylene-α-olefin copolymer cannot accomplish the object of the present invention if it has MI falling outside the above defined range. In other words, when MI of the propylene-α-olefin copolymer is either less than 3.0 or greater than 4.5, MI of the entire adhesive composition is affected, rendering the adhesive composition undesirable as an adhesive. An adhesive composition having too small MI exhibits a deteriorated fluidity and exhibits insufficient filling properties leading to the drop of adhesivity. On the contrary, an adhesive composition having too great MI can easily flow out, stay little at necessary sites and stain unnecessary sites.

[0021]

The ratio of base polymer to propylene-α-olefin copolymer in the adhesive composition is from 80/20 to 30/70 (by weight). When the proportion of the polymer grafted with a silane compound as a base polymer exceeds the above defined range, sufficient heat distortion temperature cannot be obtained. On the contrary, when the proportion of the propylene-α-olefin copolymer exceeds the above defined range, sufficient adhesivity cannot be obtained.

[0022]

The silane compound-grafted polymer and the propylene-α-olefin copolymer are nonmiscible with each other. The dispersed state of the two components has a great effect on the properties and heat distortion resistance of the adhesive. In the present invention, a propylene-α-olefin copolymer is dispersed in admixture with a silane compound-grafted polymer

as a base polymer to form a disperse phase having an average particle diameter of not greater than 80 μm, preferably not greater than 30 μm.

[0023]

In order to predetermine the diameter of the disperse phase of propylene-α-olefin copolymer to not greater than 80 μm, the conditions of mixing of the two polymers should be considered important. For example, when the two polymers are mixed at a temperature slightly lower than the melting point of the propylene-α-olefin copolymer over a two-roll mill for about 10 minutes, the resulting product has the propylene-α-olefin copolymer dispersed in the silane compound-grafted polymer, but the diameter of the disperse phases made of the copolymer is about 100 μm on the average. The composition thus obtained is very brittle and undergoes whitening and cracking when bent in the form of sheet having a thickness of 2 mm. On the contrary, when the two polymers are mixed at a temperature of 5 to 10°C higher than the melting point of the propylene-α-olefin copolymer over a two-roll mill or twin-screw mixer, the diameter of the disperse phase made of the copolymer is 80 μm or less at maximum. As the diameter of the disperse phase decreases, the heat distortion resistance of the composition improves. Further, when bent in the form of sheet, the composition undergoes whitening and cracking to an acceptable extent. The results of these studies show that the diameter of the disperse phase made of propylene-α-olefin copolymer is preferably not greater than 30 μm.

[0024]

When heated to a temperature of not lower than the melting

point of the propylene-α-olefin copolymer, the adhesive composition of the present invention exhibits a good fluidity and almost the same adhesivity to glass as the silane compound-grafted polymer itself. This is presumably because when the adhesive composition of the present invention comes in contact with glass, the silane compound-grafted polymer, which has an affinity for glass, is oriented on the surface of glass while the propylene-α-olefin copolymer forms a domain inside the surface of glass.

[0025]

Another important characteristic of the adhesive composition of the present invention is humidity resistance. In general, the adhesivity of an adhesive drops at a high temperature and humidity. The adhesive composition of the present invention has a disperse phase made of a hydrophobic propylene-α-olefin copolymer present therein and thus can inhibit the permeation of humidity therethrough. In practice, the adhesive composition of the present invention shows less change of adhesivity after 1 week of storage at a temperature of 90°C and a humidity of 95% than the silane compound-grafted polymer itself. By contrast, adhesive compositions comprising a polyethylene or polyester elastomer incorporated therein show a drastic drop of adhesivity.

[0026]

[Example]

The present invention will be further described in the following examples and comparative examples, but the present invention should not be construed as being limited thereto.

[0027]

[Examples 1 - 5; Comparison Examples 1 - 6]

As an adhesive for glass there was used a silane

compound-grafted EVA having a melting point of 92°C, a glass transition temperature of 45°C and MI of 4.5 which was then blended with a propylene-α-olefin copolymer, a polyester elastomer or a high density polyethylene (HDPE) at mixing ratios set forth in Table 1. These blends were then each kneaded under the temperature conditions set forth in Table 1 using a two-roll mill or twin-screw mixer for 10 minutes to obtain adhesive compositions. The adhesive compositions thus obtained were each evaluated for physical properties. The results are set forth in Table 1.

[0028]

The method for measuring physical properties is as follows:

<Heat distortion starting temperature (TMA)>

The various adhesive compositions were each used in an amount of from 10 to 85 mol-% to prepare sheets having a thickness of 1 mm which were each then measured for heat distortion starting temperature at an applied load of 15 g, a temperature of from room temperature to 150°C and a temperature rising rate of 10°C/min using a TMA meter produced by Shimadzu Corp.

[0029]

<Adhesivity>

Two sheets of glass plates were stuck to each other with an adhesive composition sheet having a size of 20 mm x 10 mm at a temperature of 190°C under pressure. The laminate was then measured for shear peeling strength at a pulling rate of 50 mm/min.

[0030]

<Humidity resistance>

Similarly to the aforementioned testing method, two sheets of glass plates were laminated to prepare a test specimen. The test specimen was allowed to stand in a 90°C-95% constant

temperature and humidity tank for 1 week, and then measured for shear peeling strength.

<External appearance of sheet>

The adhesive (composition) sheet was bent at an angle of 180°, and then observed for external appearance.

<Diameter of disperse phase>

For the determination of diameter of disperse phase, the composition was sliced to a small thickness. The sample thus obtained was then measured for diameter of disperse phase under optical microscope.

[0031]

The polymers set forth in Table 1 have the following properties.

(*1) Propylene-α-olefin copolymer

Melting point: 152°C, MI: 4.0 (190°C)

(*2) Propylene-α-olefin copolymer

Melting point: 141°C, MI: 1.7 (190°C)

(*3) Polyester elastomer

Melting point: 170°C

(*4) HDPE

Melting point: 132°C

[0032]

Table 1

	Example Nos.					Comparison Example Nos.					
	1	2	3	4	5	1	2	3	4	5	6
Adhesive for silane compound-grafted EVA-based glass	80	70	50	70	30	70	50	70	100	80	20
Propylene-α-olefin copolymer (*1)	20	30	50	30	70	-	-	30	-	-	80
Propylene-α-olefin copolymer (*2)	-	-	-	-	-	-	-	-	-	20	-
Polyester elastomer (*3)	-	-	-	-	-	30	-	-	-	-	-
HDPE (*4)	-	-	-	-	-	-	50	-	-	-	-
Mixing method	Twin-screw	Twin-screw	Twin-screw	Two-roll	Twin-screw	Twin-screw	Twin-screw	Two-roll	Two-roll	Twin-screw	Twin-screw
Temperature (°C)	180	180	180	160	180	180	180	160	160	180	180
Adhesivity (Kg/cm^2)											
Room temp.	51	48.5	44	47.1	43.5	36.6	21.3	42.5	45	37	16.3
150°C	12.1	10.2	9.8	8.7	7.1	1.9	1.5	6.7	2.6	6.7	0.9
After humidity resistance test	52.5	47.2	45.3	46.0	40.1	28.4	17.7	42.7	39.5	41.3	13.5
Heat distortion starting temperature (TMA) (°C)	135	138	145	116	146	83	76	85	65	138	148

External appearance of sheet (judged when bent at 180°)	Not whitened, cracked	Not whitened, cracked	Not whitened, cracked	Not whitened, cracked	Not whitened, cracked	Not whitened, cracked	Not whitened, cracked	Whitened, cracked	Not whitened, cracked	Not whitened, cracked	Whitene, cracked
Diameter of disperse phase (μm)	28	21	17	68	51	110	10 or less	96	-	23	18

[0033]

As can be seen in Table 1, the adhesive composition of the present invention is excellent all in high temperature adhesivity, heat distortion resistance and humidity resistance.

[0034]

[Advantage of the Invention]

In accordance with the present invention, an adhesive composition excellent high temperature adhesivity, heat distortion resistance and humidity resistance can be provided. The adhesive composition of the present invention is suitable for use in an art where it is required that glass plates be laminated or glass parts be retained with a high precision particularly at high temperature and humidity.